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CORROSION/EROSION BEHAVIOR OF

SILICON NITRIDE AND

SILICON CARBIDE CERAMICS -

GAS TURBINE EXPERIENCE

R. NATHAN KATZ

CERAMICS RESEARCH DIVISION

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ARMY MATERIALS AND MECHANICS RESEARCH CENTER
Watertown, Massachusetts 02172

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ABSTRACT

Ceramic materials, silicon nitride and silicon carbide in particular, are under intensive engineering development for gas turbine applications. One of the factors which has encouraged this line of development is the excellent corrosion/erosion behavior of these ceramics. This paper will briefly review some of the fundamental mechanisms and critical materials properties thought to govern the corrosion/erosion behavior of ceramics and point out where these differ from those of metals. A review of available erosion, corrosion, and combined corrosion/erosion testing of silicon nitrides and silicon carbides will be presented. While the results of these tests are quite encouraging it is evident that there is a lack of data at high temperatures, in atmospheres containing multiple contaminates, and there is virtually no long-duration testing information. The author will suggest areas of research required to further our understanding of corrosion/erosion behavior and phenomena, and provide a more extensive data base for future engineering applications.

CONTENTS

INTRODUCTION

The energy problem, environmental concerns, and strategic materials supply considerations are the driving forces behind the current emphasis on developing ceramic components for high temperature energy conversion systems. Progress over the past 10-20 years in the ability to handle complex stress analysis problems (i.e., finite element techniques and more powerful computers) has provided a reasonable level of confidence that successful design with brittle materials, such as ceramic, in structural applications is now possible. Similarly, improved quality, high strength, high temperature capability ceramic materials with low thermal expansions (required to minimize materials stress due to extreme thermal transients) are now available. In particular, two families of engineering materials, one based on silicon nitride and one based on silicon carbide, are under intensive engineering development for use in gas turbines and diesel engines.[1-3]

One of the factors frequently cited for selection of a given silicon nitride (Si_3N_4) or of a given silicon carbide (SiC) for a specific gas turbine hot flow path component is corrosion/erosion resistance. However, when one examines the literature it is rapidly apparent that in fact very little data is available to support this assumption. Fortunately, the largely successful testing of components fabricated from these materials in engine test rigs and in actual engines is supporting the engineering judgment which lead to their utilization. Nevertheless, anticipated requirements for engines to operate for 7,500 to 30,000 hours time between overhaul (TBO) go substantially beyond any prudent extrapolation which can be made from current corrosion/erosion data base. Indeed, there is not sufficient experience in the use of ceramics in highly stressed applications at high temperatures to even know how to make such an extrapolation, prudent or otherwise! The emphasis throughout this paper on the necessity for measuring retained strength after environmental exposures is founded on the need for such an experience base. It is of particular importance in designing with brittle materials to know how environmental explosure will affect strength, as small changes in strength will have large effects on component reliability and life.

A major difficulty in obtaining a meaningful data base on the corrosion/ erosion behavior of ceramics (or indeed any material) is that it is extremely difficult to reproduce in the laboratory the complex superposition of phenomena which a material will see in actual service. The complex interplay of stress and temperature gradients, varying gas or fluid flows, and the random nature of dust and impurity ingestion varies from engine to engine, making it difficult to devise one universal laboratory test which will predict engine experience. Nevertheless, by breaking the complex environmental exposure phenomena into their simpler components (i.e., erosion, oxidation, corrosion, etc.), one can gain insight into how a material may behave in the more complex environment. However, it is important to verify such predictions of behavior with rig or systems tests which reproduce the complex environment which the material will actually see.

1. BURKE, J. J., GORUM, A. E., and KATZ, R. N., ed. *Ceramics for High Performance Applications.* Brook Hill Publishing Co., Chestnut Hill, Massachusetts, 1974.
2. BURKE, J. J., LENOE, E. M., and KATZ, R. N., ed. *Ceramics for High Performance Applications - II.* Brook Hill Publishing Co., Chestnut Hill, Massachusetts, in-press.
3. *Proceedings: Workshop on Ceramics for Advanced Heat Engines.* Energy Research and Development Administration, Division of Conservation Research and Technology, Report Conf-770110, January 1977.

This paper will review the current data base on the corrosion/erosion of Si₃N₄- and SiC-based ceramics from the above perspective. We will first review the status of laboratory studies of two phenomena which are relevant to corrosion/erosion behavior, namely erosion and oxidation. Laboratory-scale corrosion/erosion studies in both clean and contaminated combustion environments will be reviewed. Limited data on the effect of environemntal exposure on retained strength will be presented. Corrosion/erosion behavior which may be inferred from engine rig testing of Si₃N₄ or SiC components in an actual combustion gas environment will be discussed. Further inferences will be made from experiences with Si₃N₄ and SiC components in engines. Finally, an assessment of gaps in the existent corrosion/erosion data base will be presented.

Because most of the data presented in this paper is derived from gas turbine oriented programs, the materials behaviors cited were obtained in air, O_2, or oxygen-rich combustion environments. Corrosion/erosion behavior in reducing environments is likely to be vastly different, and no inference on the behavior of SiC or Si₃N₄ in reducing environments should be drawn.

EROSION

Only solid particle erosion will be considered. An extensive literature on liquid droplet erosion exists, and interested readers are referred to References 4 and 5. The phenomenology of the solid particle erosion behavior of metals and ceramics are significantly different as illustrated schematically in Figure 1.
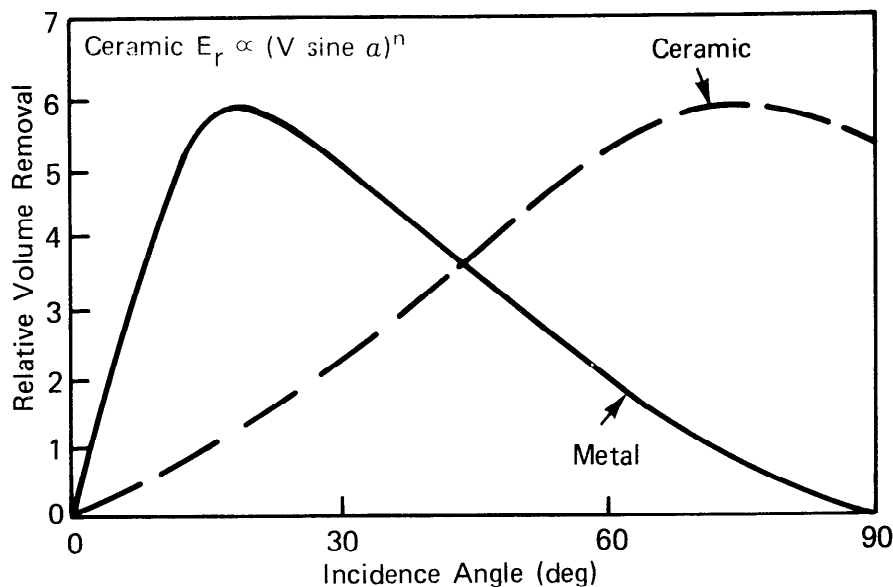

Figure 1. Comparison of ceramic versus metallic particulate erosion resistance behavior.

4. FIELD, J. E., CAMUS, J. J., GORHAM, D. A., and RICKERBY, D. G. *Proceedings of 4th International Conference on Rain Erosion.* Meersburg, 1974.
5. FIELD, J. E., CAMUS, J. J., GORHAM, D. A., and RICKERBY, D. G. *High Speed Liquid Impact Studies.* DRMAT Report 203, HMSO London, 1976, (also AD A043158).

A particle impingement angle of 15 to 20° results in a maximum erosion rate for metals, whereas this is a relatively benign situation for a typical ceramic. The maximum erosion rate for ceramics occurs at 90° impingement.[6] In general, erosive wear of ceramics follows an empirical equation of the form:

$$E_r \propto (V \sin \alpha)^n \tag{1}$$

where E_r is erosion rate, V is particle velocity, α is the impingement angle and n is an empirically determined exponent.[6] It has also been found that E_r is proportional to the ceramics hardness and fracture toughness. Hockey et al.[6] have recently carried out an in-depth investigation of the role of these variables in the solid particle erosion of strong ceramics, including silicon nitride. However, it is more useful for the purposes of this paper to cite data from studies where comparisons between metals and ceramics can be made, or amongst substantially differing ceramics, even if the data is less extensive.

The results of one such study, conducted by Solar Division of International Harvester under contract to the U.S. Army Mobility Equipment Research and Development Command, are shown in Tables 1 and 2. It is apparent that the worst performing ceramic, reaction-bonded silicon nitride (RBSN), a material with about 20 to 25% porosity, is approximately equal to the superalloy in performance and that the hot-pressed Si_3N_4 (HPSN) and SiC are about an order of magnitude better. These data influenced the selection of HPSN for application as an erosion-resistant nozzle vane in a Solar/MERADCOM 10 kW turboalternator, which will be discussed in more detail in this paper.

Table 1. EROSION OF CANDIDATE NOZZLE MATERIALS VERSUS IMPINGEMENT VELOCITY

Material	Impingement Angle, Degree	Mean Particle Impingement Velocity, fps		
		190	520	840
		Erosion Volume Loss × 10^3 cc		
713 LC Superalloy	30	0.09	2.60	-
	90	0.21	1.79	30.0 26.8
Hot-Pressed Silicon Nitride	90	-	0.12	0.22 0.63 0.56
Hot-Pressed Silicon Carbide	90	-	0.32	1.59 1.28 1.34
Recrystallized Silicon Carbide, Silicon Filled (NC-430)	90	0	0.39	2.34 3.08
Reaction-Bonded Silicon Nitride	90	0	2.88	21.7 28.2

Test Conditions: 15 minutes at room temperature with 80 mg/ft³ of 43-74 micron Arizona road dust and 3/8 in. (0.95 cm) diameter nozzle. Gas velocity 200 fps (1.90), 600 fps (520), 1000 fps (840).
Data obtained at Solar under Contract DAAK02-75-C-0138.

6. HOCKEY, B. J., WIEDERHORN, S. M., and JOHNSON, H. *Erosion of Brittle Materials by Solid Particle Impact*. National Bureau of Standards Report NBSIR-77-1396, December 1977.

Table 2. EROSION OF CANDIDATE NOZZLE MATERIALS VERSUS IMPINGEMENT ANGLE

Material	Erosion Volume Loss × 10^3 cc 30-Degree Impingement Angle	Erosion Volume Loss × 10^3 cc 90-Degree Impingement Angle
713 LC Superalloy	2.60	1.79
Hot-Pressed Silicon Nitride	0	0.12
Hot-Pressed Silicon Carbide	0.04	0.32
Reaction-Bonded Silicon Nitride*	1.65†	2.88
NC-430	0.08	0.39

*Ground Surface
†Derived from previous results
(520 fps mean particle impingement velocity, 15 minutes at room temperature, 80 mg/ft^3 of 43-74 micron Arizona road dust and 3/8 in. (0.95 cm) diameter nozzle.)
Data obtained at Solar under Contract DAAK02-75-C-0138.

As part of a program to utilize ceramics in helical expander Brayton cycle turbomachines for coal-fired topping cycles, Myers el al.[7] have acquired data on the relative resistances of various ceramics to both fly ash and alumina particulates. The results of these room temperature tests are shown in Figure 2. Subsequently, erosion tests of HPSN, HPSiC, and Crystar-sintered SiC were conducted in a 1360 C combustion gas steam containing 6 g/min of coal fly ash impinging at 100 M/S. Erosion was not a problem; ash build-up was!

★Ash ~ 1 μg/g
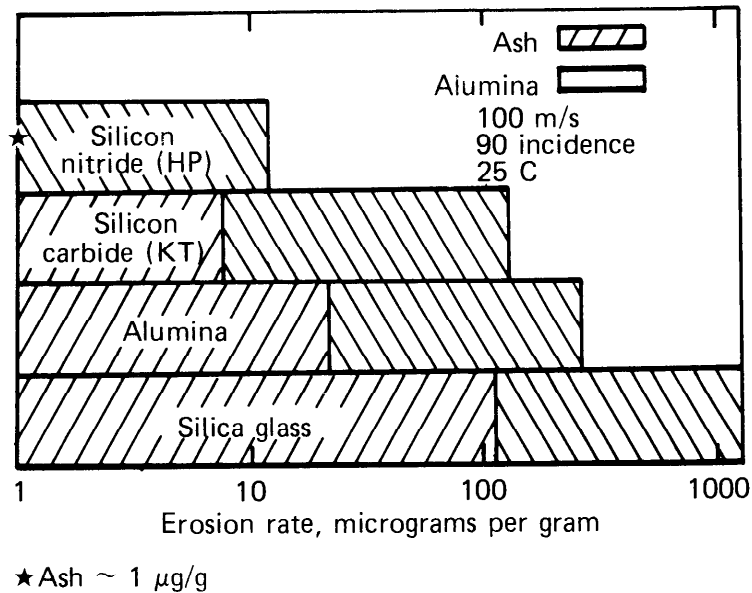
Figure 2. Erosion rate of ceramics by ash one-tenth the rate using alumina (after Meyers et al., Reference 7).

7. MEYERS, B., LANDINGHAM, R., MOHR, P., and TAYLOR, R. An Adiabatic Coal-Fired 1350 C Expander in Proceedings: Workshop on Ceramics for Advanced Heat Engines, Energy Research and Development Administration, Division of Conservation Research and Technology, January 1977, p. 151-160.

Some data on the retained strength after erosive exposure has been obtained by Gulden[8] on HPSN, RBSN, and glass-bonded Al_2O_3. Natural quartz of varying particle size was impacted at 90° impingement angle on test samples; velocities were apparently varied during the testing. Gulden noted a trend toward strengthening after erosion sufficient to remove 31 μm from the surface ($\sim 3 \times 10^8$ impacts on a 0.71 cm^2 area). The basis for this conclusion was that after erosion 50% of the test bars (3 point MOR) broke at stresses greater than 1 standard deviation above the pre-erosion controls. The other 50% broke within 1 standard deviation and no samples broke below 1 standard deviation. She attributes this beneficial result to a polishing phenomena. There seems to be a similar but less conclusive bias for the eroded glass-bonded Al_2O_3 to fracture more frequently above 1 standard deviation than below 1 standard deviation. On the other hand, her data show that RBSN subjected to the same test erodes ~ 360 μm and shows a strong tendency toward strength reduction.

OXIDATION

Singhal[9] has recently carried out a thorough study of the thermodynamics of dissociation of Si_3N_4 and SiC as a function of O_2 partial pressure and temperature, as well as the stability of the protective SiO_2 surface layer which forms on both materials in the presence of oxygen. Basically, as long as O_2 partial pressures representative of gas turbine environments are present, both materials are stable to well beyond 1600 K, indeed, the surface SiO_2 is stable to 2000 K. However, the protective SiO_2 layer can be maintained only down to $\sim 4 \times 10^{-4}$ atmosphere of O_2 at 1600 K and $\sim 2 \times 10^{-1}$ atmosphere of O_2 at 2000 K. Below these, "active" oxidation can occur. Similarly, in reducing environments or in vacuums, SiO_2 can break down into SiO and O_2, removing the protective oxide. Thus Si_3N_4 and SiC can be used in reducing environments only at relatively low temperatures. In real systems, however, densification aids, second phases, and porosity can significantly modify the oxidation behavior. In any event, oxidation rate data provides insight only as to whether or not the material will be dimensionally or phase stable, and doesn't give any information as to properties. Therefore, rather than present oxidation rate data we will review the effect of oxidation in "uncontaminated" air on strength where possible.*[10]

Miller et al. have obtained data on the effect of long-term oxidation on the retained strength of HS 130 (the predecessor of NC 132), hot-pressed silicon nitride, and NC 203 silicon carbide. The results for HS 130 (Figure 3a) show that retained strength is significantly degraded after long-term oxidation at 2500 F, even at temperatures as high as 2300 F. This strength reduction is attributed to surface pitting at the Si_3N_4/SiO_2 interface. The results for NC 203 (Figure 3b)

*Those who are interested in oxidation rate data for silicon nitrides and carbides are referred to the excellent review paper by Sims & Palko[10] as well as Singhal's work.[9]

8. GULDEN, M. E. *Study of Erosion Mechanisms of Engineering Ceramics.* Solar Turbines International, 6th Interim Report on Contract N00014-73-C-0Y01, August 1977.

9. MILLER, K. G., et al. *Brittle Materials Design, High Temperature Gas Turbine - Materials Technology.* Westinghouse, Contract DAAG46-71-C-0162, Final Report, AMMRC CTR 76-32, v. 4, December 1976.

10. SIMS, C. T., and PALKO, J. E. *Surface Stability of Ceramics Applied to Energy Conversion Systems* in Proceedings: Workshop on Ceramics for Advanced Heat Engines, Energy Research and Development Administration, Division of Conservation Research and Technology, January 1977, p. 287-294.
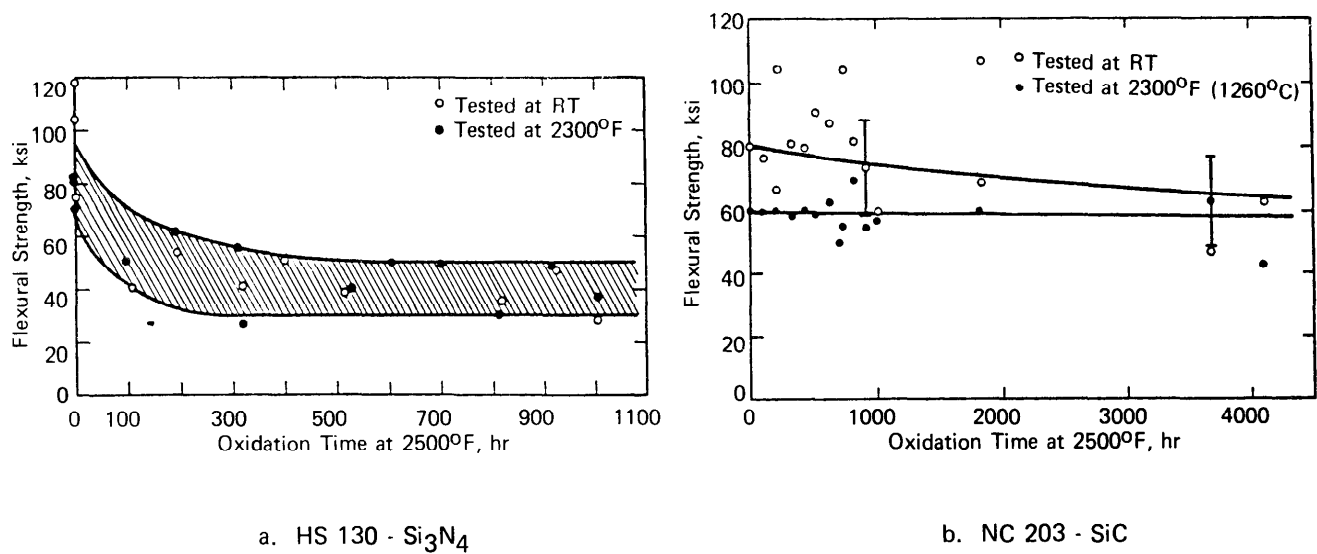
a. HS 130 - Si₃N₄

b. NC 203 - SiC

Figure 3. Retained strength after 2500 F oxidation of hot-pressed Si$_3$N$_4$
and SiC at RT and 2300 F (Reference 9).

show slight degradation of RT strength and no degradation of 2300 F strength, even with exposure to 4000 hours. The strength reduction in the RT tests is attributed to cracking of the SiO$_2$ surface layer on cooling.

The above results are for fully dense hot-pressed materials. Reaction-bonded silicon nitride is also known to undergo appreciable strength loss on static oxidation. The amount of oxidation and resultant strength loss are functions of both the oxidation temperature and density (porosity) of the RBSN material, as shown by the results of Mangels (Table 3).[11] These results are in agreement with earlier work reported by Godfrey.[12] The author is unaware of comparable data on the effect of simple O$_2$ or air exposure at high temperatures

Table 3. RETAINED STRENGTH AFTER OXIDATION OF FORD RBSN
(After Mangels, Reference 11)

Density	Oxidation Temperature, Deg C	Exposure Time, Hr	ΔWt, %	RT-Retained MOR, MN/m²	Changes in MOR, %
2.55 g/cc	-	-	-	245	-
	1038	200	+3.7	195	-25
	1260	200	+2.0	135	-46
2.7 g/cc	-	-	-	275	-
	1038	200	+0.75	275	0
	1260	200	+0.55	215	-22

11. MANGELS, J. A. *High Temperature, Time Dependent Physical Property Characterization of Reaction Sintered Si₃N₄* in Nitrogen Ceramics, F. L. Riley, ed., Noordhoff, 1977, p. 589-593.
12. GODFREY, D. J., and PITMAN, K. C. *Some Mechanical Properties of Si₃N₄ Ceramics: Strength, Hardness and Environmental Effects* in Ceramics for High Performance Applications, J. J. Burke, A. E. Gorum, and R. N. Katz, ed., Brook Hill Publishing Co., Chestnut Hill, Massachusetts, 1974, p. 425-444.

on the retained strength of reaction-bonded or sintered silicon carbides. However, many components of "Crystar," REFEL, or KT type of SiC's have been known to survive in highly stressed environments for long times. Some of this experience will be discussed subsequently in this paper.

The fact that both fully dense and reaction-bonded silicon nitrides can lose about half of their strength after several hundred hours of static oxidation while fully dense silicon carbide seems to be unaffected is an important basis of comparison for the results in the more complex testing environments which follow.

CORROSION/EROSION

A. Relatively Clean Environments

Work by investigators at Westinghouse documented in the ARPA "Brittle Materials Design" program final report[9] provides data on corrosion/erosion behavior of HS 130 and NC 203 materials in a 3 atm. combustor rig burning Exxon #2 diesel fuel. This fuel was barium free and had: 0.35 w/o (max) S; 0.01 w/o (max) ash; and 0.2 w/o (max) carbon residue. Results of 250-hour test programs for 2000 F and 2500 F exposures are shown in Figures 4a and b. The effect of these exposures on retained strength at 2000 F (1100 C) are presented in Figure 5 and Table 4. No room temperatures retained strength data are available. It is evident from Figure 5 that exposures at 2000 F had no effect on strength at 2000 F. (Miller et al. note some effect on longer duration testing.) Strengths of both materials at 2000 F are severely degraded by the 2500 F exposures.

B. Contaminated Environments

To the best of this author's knowledge there is no published data on the effect of Na, S, V, Pb or other fuel contaminants on the strength (retained or

a. Corrosion/erosion behavior of hot-pressed silicon carbide and silicon nitride in turbine passage at 2000 F, 3 atm. pressure and 152 m/s gas velocity using Exxon No. 2 diesel oil.

b. Corrosion/erosion behavior of hot-pressed silicon nitride in turbine passage at 2500 F, 3 atm. pressure and 500 ft/sec gas velocity using Exxon GT-2 oil.
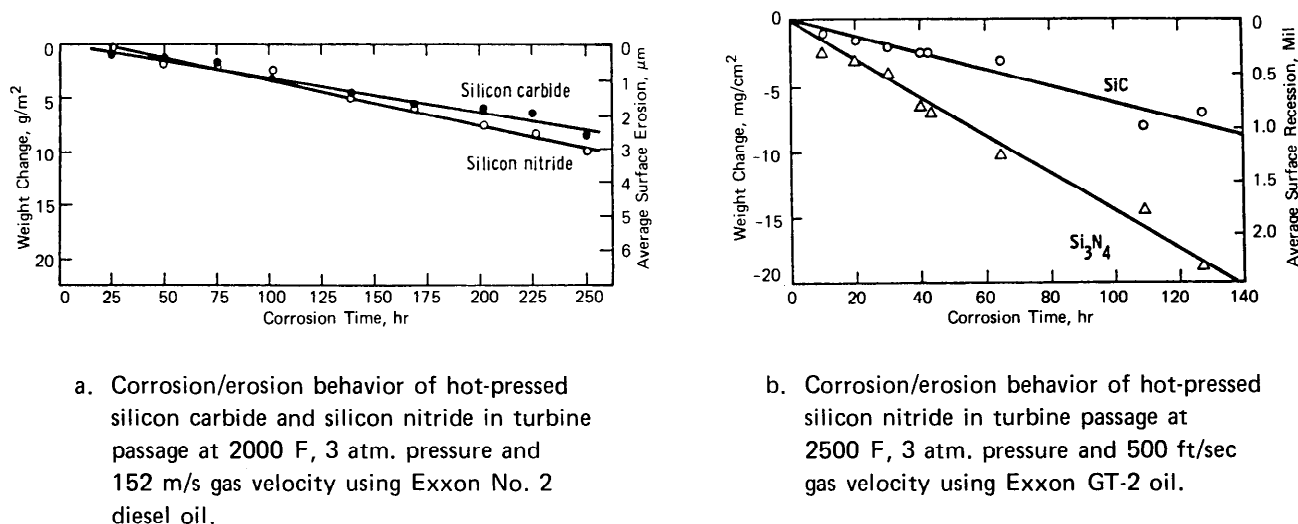
Figure 4. Corrosion/erosion behavior of hot-pressed SiC and Si_3N_4 (Reference 9).
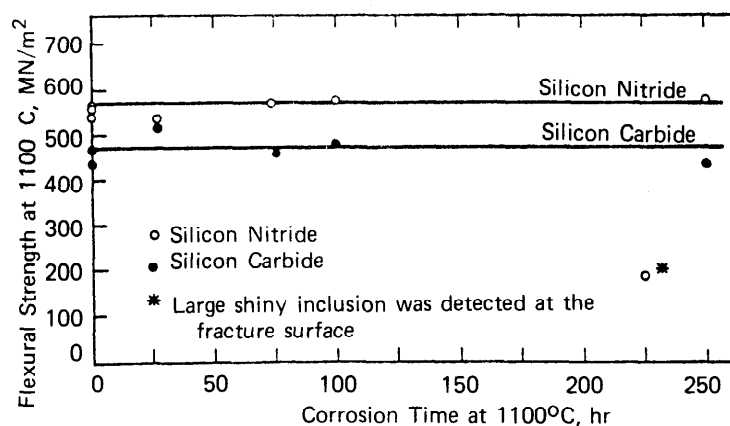
Figure 5. Effect of gas turbine environment on the flexural strength
of hot-pressed Si_3N_4 and SiC (Reference 9).

Table 4. EFFECT OF CORROSION/EROSION AT
2500 F AND 3 ATM. PRESSURE ON
FLEXURAL STRENGTH AT 2000 F
(Reference 9)

Time (hr)	Si_3N_4 (ksi)	SiC (ksi)
0	80	65
10	65	55
20	65	56
30	63	52
40	63	57
43	60	55
65	54	52
109	57	55
127	51	51

during exposure) of silicon nitrides on carbides (except for the work of Richerson
and Yonushonis[13] to be noted below in the section of cyclic oxidation). This
data will be briefly reviewed by type of contaminant.

1. Na and S - Hot Corrosion

Gas turbine engineers refer to the corrosion caused by the joint attack of
Na and S as hot corrosion. Sims and Palko[10] have recently reported on hot corro-
sion studies on several Si_3N_4 and SiC carried out by themselves, and others.
Their results, shown in Figure 6, indicate that except for the oil-fired boiler
data (a heavy slagging environment) the ceramics seem to perform much better than
the super alloys. It is important to note that some of the G.E. tests go to
10,000 hr at 1600 F.

Schlichting[14] has recently reported on his studies of the hot corrosion of
Si_3N_4 and SiALON (a solid solution of Al_2O_3 in β' silicon nitride plus various

13. RICHERSON, D., and YONUSHONIS, T. *Environmental Effects on the Strength of Si_3N_4 Materials* in Proceedings of the 1977
DARPA/NAVSEA Ceramic Gas Turbine Review, MCIC 78-36, March 1978.
14. SCHLICHTING, J. *Oxidation and Hot Corrosion Behavior of Si_3N_4 and SiALON* in Nitrogen Ceramics, F. L. Riley, ed., Noordhoff,
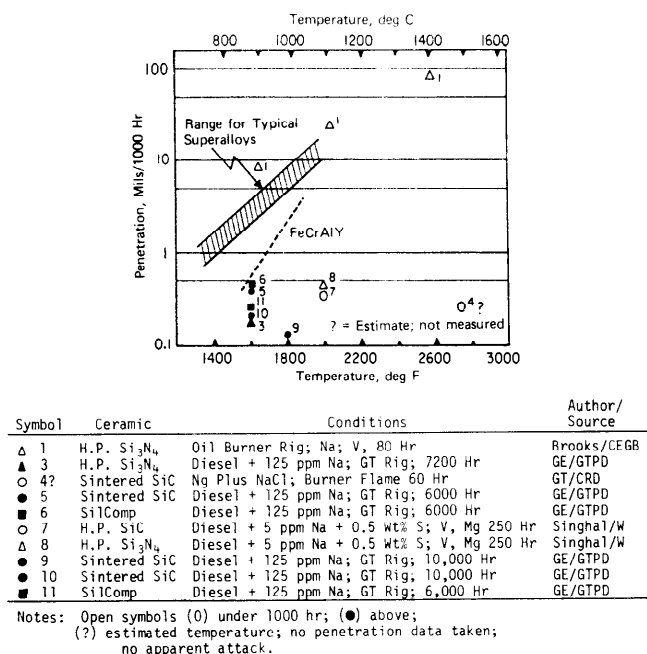1977, p. 627-634.

**Figure 6. Corrosion behavior of ceramics
(after Sims & Palko, Reference 10).**

Symbol	Ceramic	Conditions	Author/Source
Δ 1	H.P. Si₃N₄	Oil Burner Rig; Na; V, 80 Hr	Brooks/CEGB
▲ 3	H.P. Si₃N₄	Diesel + 125 ppm Na; GT Rig; 7200 Hr	GE/GTPD
○ 4?	Sintered SiC	Na Plus NaCl; Burner Flame 60 Hr	GT/CRD
● 5	Sintered SiC	Diesel + 125 ppm Na; GT Rig; 6000 Hr	GE/GTPD
■ 6	SilComp	Diesel + 125 ppm Na; GT Rig; 6000 Hr	GE/GTPD
○ 7	H.P. SiC	Diesel + 5 ppm Na + 0.5 wt% S; V, Mg 250 Hr	Singhal/W
Δ 8	H.P. Si₃N₄	Diesel + 5 ppm Na + 0.5 Wt% S; V, Mg 250 Hr	Singhal/W
● 9	Sintered SiC	Diesel + 125 ppm Na; GT Rig; 10,000 Hr	GE/GTPD
● 10	Sintered SiC	Diesel + 125 ppm Na; GT Rig; 10,000 Hr	GE/GTPD
■ 11	SilComp	Diesel + 125 ppm Na; GT Rig; 6,000 Hr	GE/GTPD

Notes: Open symbols (○) under 1000 hr; (●) above;
(?) estimated temperature; no penetration data taken;
no apparent attack.

second phases). The tests were performed in a burner rig (fuel unspecified) cycling between 1000 and 1200 C. Sodium chloride and H_2S added into the burner gas were found not to corrode the ceramics. The presence of compounds which form alkali melts in which a surface sodium silicate glass may dissolve the Si_3N_4, such as Na_2SO_4 or Na_2CO_3, do cause hot corrosion. However, as is shown in Figure 7, RBSN is several times more resistant to hot corrosion than is the superalloy tested; and the SiALON is more than an order of magnitude more resistant. Schlichting points out that controlling the Na_2O content of the contaminant will significantly increase the ceramic lifetime.
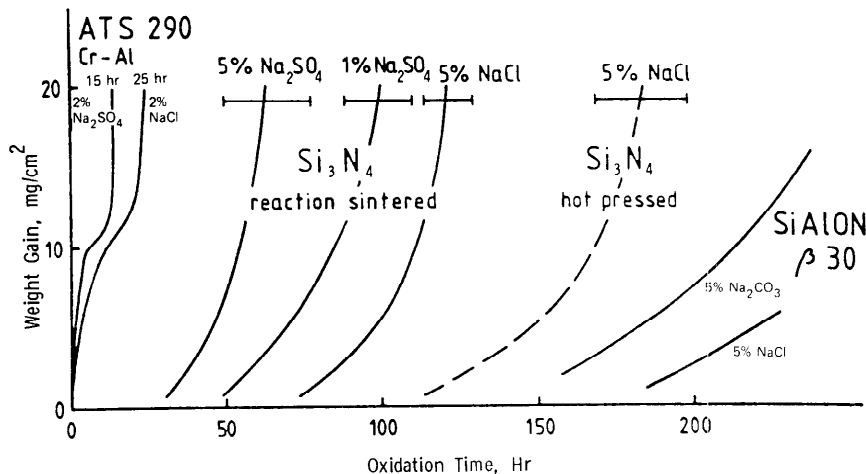

Figure 7. Corrosion of Si_3N_4, SiALON and a Cr-aluminized superalloy in burner gas under cycling conditions (after Schlichting, Reference 14).

9

2. Vanadium

Schlichting[14] studied the addition of V_2O_5 to the burner gas stress described above. He observed little dissolution (corrosion) of Si_3N_4 or SiALON's in this environment. Investigators at Westinghouse[15] have examined the combined effects of S, Na, V, and Mg on the behavior of HS 130 and NC 203 at 2000 F as shown in Figures 8a and b. Impurities seem to affect the corrosion/erosion behavior of HS 130 but not NC 203. However, the maximum weight gains after 250 hours are similar for both materials.

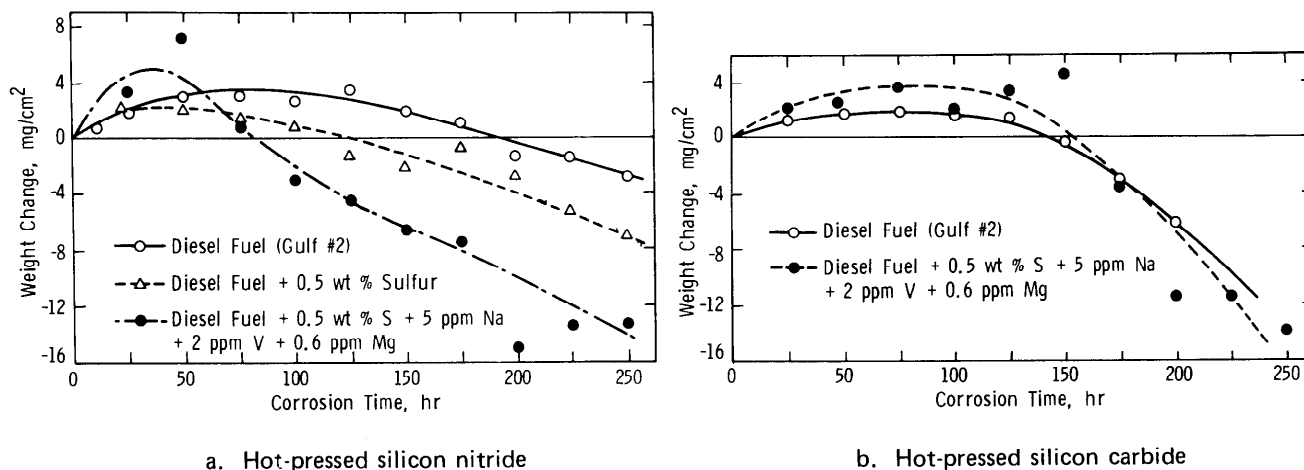a. Hot-pressed silicon nitride   b. Hot-pressed silicon carbide

Figure 8. Effect of fuel contaminants on the corrosion of hot-pressed silicon nitride and hot-pressed silicon carbide in a turbine test passage at 2000 C and 3 atm. pressure (Reference 15).

3. Lead

Under the vehicular portion of the ARPA "Brittle Materials Design" program, Ford Motor Co. had samples exposed to lead in the Westinghouse combustion rig.[16] Clean research gasoline to which 0.50 gram per gallon of tetraethyl lead were added was used. Tests were run at 500 ft/sec, at 3 atm., and 2000 F for 45 hours. Results of these tests are shown in Table 5. No evidence was found that would suggest that the lead produced any deleterious effects. However, it was recognized that mechanical property testing after exposure would be required to substantiate the absence or presence of deleterious effects.

CYCLIC OXIDATION

In addition to the essentially isothermal oxidation or hot gas exposure investigations cited above, there have been two studies of the effect of combined thermal cycling and thermal exposure on the retained strength of silicon-based ceramics.

15. McLEAN, A. F., FISHER, E. A., and BRATTON, R. J. Brittle Materials Design, High Temperature Gas Turbine. Ford Motor Co., Contract DAAG46-71-C-0162, Interim Report, AMMRC CTR 73-9, March 1973, p. 162-164.
16. McLEAN, A. F., BAKER, R. R., BRATTON, R. J., and MILLER, D. G. Brittle Materials Design, High Temperature Gas Turbine. Ford Motor Co., Contract DAAG46-71-C-0112, Interim Report, AMMRC CTR 76-12, April 1976, p. 78-93.

Table 5. EFFECT OF LEAD ON WEIGHT GAIN AT 2000 C AND
3 ATM. FOR Si_3N_4 AND SiC IN A TURBINE TEST PASSAGE
(Reference 16)

	Specimen	Original Weight, gm	Final Weight, gm	Change in Weight, gm
1.	Norton NC 203 SiC	6.79410	6.79714	+0.00304
2.	Norton HS 130 Si_3N_4	6.55480	6.56077	+0.00597
3.	Norton HS 130 Si_3N_4	6.56375	6.56973	+0.00598
4.	Ford Reaction-Sintered Si_3N_4	3.46510	3.66340	+0.19830
5.	Ford Reaction-Sintered Si_3N_4	3.45564	3.67054	+0.21490

One study was conducted by Richerson and Yonushonis at AiResearch,[13] the other is being carried out at AMMRC.[17] These will be briefly described in turn. (The AiResearch tests[13] will be extended to longer times under a recently initiated DOE Contract #DEN 3-27.)

A. AiResearch Cyclic Oxidation Studies

Richerson and Yonushonis[13] evaluated NC 132 HPSN, NC 350 RBSN, and an experimental grade of HPSN, NCX 34. They utilized a combustor rig burning jet A fuel. In addition to the effect of cyclic oxidation, they included the effect of specimen grinding direction in their studies. Tables 6 through 8 present their data. This data is of particular importance in that it is the only data showing the effect of Na on retained strength.

For NC 132, a fully dense hot-pressed Si_3N_4, the control data clearly indicates that strength is a function of the orientation of stressing. Static oxidation at temperatures below ∿2000 F and for short times seemed to restore the strength of transverse ground samples. Richerson and Yonushonis attribute this to crack "healing" due to smoothing of the surface grooves. However, once temperatures of ∿2065 F and times of ∿140 hours are attained, strength degradation due to surface pitting commences. At higher temperatures or long times (i.e., 240 hours) at 2065 F, the strengths are reasonably consistent with those measured by the Westinghouse investigators. Cyclic oxidation in clean combustion environments for ∿50 hours with 2050 F max (Figure 3) temperature actually strengthened the NC 132 material. However, the injection of 5 ppm sea salt (Na) into the gas stream reduced the strength significantly, as shown in Table 6.

The NCX 34 material was developed by the Norton Co. to provide an improved high temperature strength and creep-resistant HPSN material. As is evident from Table 7 as compared to Table 6 and Figure 3, NCX 34 is also a decided improvement over NC 132 with respect to oxidation resistance.

Richerson and Yonushonis' data for NC 350 RBSN (Table 8) show that static oxidation degrades the strength of as-nitrided RBSN but not of machined RBSN. Cyclic oxidation in "clean" combustion gas may actually improve the strength of RBSN. However, again we see that 5 ppm of sea salt produces severe degradation.

17. KATZ, R. N., LENOE, E. M., and QUINN, G. D. *Review of Durability Testing of Structural Ceramics* in Highway Vehicle Systems DOE, Conf-771037, March 1978, p. 208-223.

Table 6. RETAINED RT FOUR-POINT MOR OF NORTON NC-132 HOT-PRESSED Si_3N_4
(After Richerson and Yonushonis)

Test Type	Surface Condition, Exposure	Average Strength (ksi)	Standard Deviation	Samples Tested	Predominant Fracture Region
Control	L	97	16.8	38	Surface at Variety of Flaws
	T	63	5.0	12	Surface at Grind Grooves
Static Oxidation	T, 1800 F/50 Hr	92	8.6	50	Surface, Flaws not Obvious
	T, 1950 F/50 Hr	89	5.7	11	Surface, Flaws not Obvious
	T, 2065 F/140 Hr	83	5.0	6	Surface Pits
	T, 2065 F/240 Hr	62	8.1	6	Surface Pits
	T, 2200 F/24 Hr	74	2.6	12	Surface Pits
	T, 2500 F/24 Hr	64	4.1	12	Surface Pits
Cyclic Oxidation	T, 1950 F/1 Hr, Air Quench/ 5 Min, 50 Cycles	99	12.0	4	Surface, Flaws not Obvious
	L, 2050 F/5 Min, Air Quench/ 3 Min, 100 Cycles	108	7.0	8	Surface, Flaws not Obvious
	L, 1650 F/1.5 Hr, 2050 F/0.5 Hr, Air Quench/5 Min, 25 Cycles	100	20.0	4	Surface, Flaws not Obvious
	L, Same Cycle as Above with 5 ppm Sea Salt	71	2.4	4	Surface Corrosion
	L and T, 1950 F/3 Min, 1650 F/ 5 Min, Air Quench/3 Min, 135 Cycles, 5 ppm Sea Salt	81	-	4	Surface Corrosion

L - 320 - Grit longitudinal
T - 320 - Grit transverse

Table 7. RETAINED RT FOUR-POINT MOR OF NORTON NCX-34
HOT-PRESSED Si_3N_4
(After Richerson and Yonushonis)

Test Type	Surface Condition, Exposure	Average Strength (ksi)	Standard Deviation	Samples Tested
Control	L	139	-	8
	T	100	-	3
Static Oxidation	L, 1830 F/100 Hr	156	23.5	4
	L, 1830 F/300 Hr	144	9.8	4
	L, 2010 F/100 Hr	120	8.4	4
	L, 2010 F/300 Hr	104	15.5	4
	L, 2065 F/240 Hr	116	-	3
	T, 2065 F/240 Hr	105	-	3
	L, 2190 F/100 Hr	101	6.1	4
	L, 2190 F/300 Hr	94	9.4	4
	L, 2370 F/100 Hr	94	6.0	4
	L, 2370 F/300 Hr	84	16.6	4
Cyclic Oxidation	1950 F/1 Hr, Air Quench/5 Min, 50 Cycles	150	-	3

L - 320 - Grit longitudinal
T - 320 - Grit transverse

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Table 8. RETAINED RT FOUR-POINT MOR OF NORTON NC-350 REACTION-BONDED Si_3N_4
(After Richerson and Yonushonis)

Test Type	Surface Condition, Exposure	Average Strength (ksi)	Standard Deviation	Samples Tested
Control	A	31	4.0	12
	L	31	2.7	6
	T	23	4.4	6
Static Oxidation	A, 1800 F/50 Hr	30	4.0	6
	A, 2250 F/50 Hr	20	3.6	12
	L, 2250 F/50 Hr	33	5.6	6
	T, 2250 F/50 Hr	37	3.0	6
Cyclic Oxidation	A, 1950 F/1 Hr, Air Quench/ 5 Min, 50 Cycles	36	-	6
	L, 1950 F/1 Hr, Air Quench/ 5 Min, 50 Cycles	43	4.2	6
	T, 1950 F/1 Hr, Air Quench/ 5 Min, 50 Cycles	42	5.7	6
	T, 1950 F/3 Min, 1650 F/5 Min, Air Quench/3 Min, 135 Cycles, 5 ppm Sea Salt	26	-	5
	A, 2250 F/5 Min, Air Quench/ 3 Min, 70 Cycles	34	2.8	6
	T, 2250 F/5 Min, Air Quench/ 3 Min, 70 Cycles	35	1.1	4
	A, 1650 F/1.5 Hr, 2050 F/ 0.5 Hr, Air Quench/5 Min, 25 Cycles	30	1.6	4
	A, 1650 F/1.5 Hr, 2050 F/ 0.5 Hr, Air Quench/5 Min, 25 Cycles, 5 ppm Sea Salt	17	1.7	4

A - As-Nitrided
L - 320 - Grit longitudinal
T - 320 - Grit transverse

B. AMMRC Combined Thermal Exposure/Thermal Cycling Studies

Quinn has been investigating combined high temperature exposure in air with thermal cycling, under a joint DOE/AMMRC program.[17] Three hundred and sixty hours of exposure in air at temperatures ranging between 1000 and 1371 C plus 500 thermal cycles are accumulated on each material studied according to the schedule shown in Figure 9. The thermal cycles are carried out in an oxygen-MAPP gas
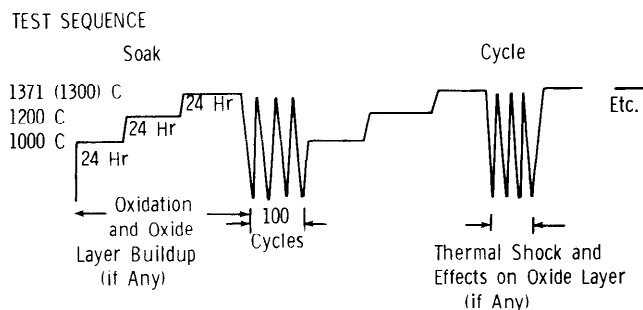
Note: Maximum temperature of 1300 C is used for SiC materials with free silicon as a constituant.

Figure 9. Combined thermal exposure/thermal cycling test sequence.

flame (clean flame) with air quenching as described in Reference 18. Silicon nitrides and silicon-free SiC's are given a maximum exposure/cycle temperature of 1371 C (2500 F); for SiC materials with free silicon such as G.E.'s SilComp the maximum temperature is 1300 C (2372 F). "Virgin" materials properties (4-point modulus of rupture and Weibull "m," both at RT) were obtained on a population of 16 samples per material. Environmentally exposed materials properties (retained strength and Weibull "m," at RT) were obtained on a population of 11 to 12 samples per material. Materials tested to date are NC 132 (HPSN), NC 203 (HPSiC), NC 350 (RBSN), KBI - RBSN, and G.E. SilComp. Quinn's results are shown in Table 9. His results on NC 132 and NC 203 are in good agreement with the Westinghouse results on oxidation exposure in air shown in Figure 3. This would indicate that the effect of thermal cycling in the manner shown in Figure 9 is less important than is the effect of oxidation exposure. Both grades of RBSN evaluated suffered ~20% strength reduction after exposure. This is less than one might have anticipated from the work of Mangels and Godfrey cited earlier. Quinn's data covers higher temperatures and longer times than the AiResearch work discussed above, therefore it is not appropriate to draw comparisons. The SilComp data is the first on the retained strength of this class of materials. Therefore, no comparisons can be made.

The important result of Quinn's work is that cyclic oxidation/flame cycling for 360 hours did degrade the properties of all the materials studied, with the exception of NC 203.

To summarize the available data based on laboratory test samples:

Si_3N_4's and SiC's exhibit outstanding (indeed, one might say unexcelled) particulate erosion resistance.

Si_3N_4's and SiC's show excellent oxidation resistance and associated shape stability in air, oxygen, and combustion gases (even with Na, S, V, and Pb).

Table 9. RETAINED STRENGTH AFTER COMBINED THERMAL
EXPOSURE/THERMAL CYCLING
(After Quinn)

Material	Virgin - RT MOR*		Exposed - Retained RT MOR[+]	
	ksi	"m"	ksi	"m"
NC-132 HPSN	104	12.4	50.5	9.6
NC-203 HP SiC	99	9.9	102	8.3
NC-350 RBSN	43	7.2	35	6.4
KBI - RBSN	30	14.8	24	14.2
SilComp - Si/SiC (G.E.)	47	6.6	32	8.8

*16 Tests per data point
[+]360-hour exposure and 500 thermal cycles,
11 to 12 tests per data point

18. QUINN. G. D., KATZ, R. N., and LENOE, E. M. *Thermal Cycling Effects, Stress Rupture and Tensile Creep in Hot Pressed Si3N4* in Proceedings of the 1977 DARPA/NAVSEA Ceramic Gas Turbine Demonstration Engine Review, MCIC 78-36, March 1978.

Si_3N_4's and, apparently to a lesser extent, SiC's can suffer major reductions in a retained strength after exposure to oxidative environments and/or under corrosion/erosion conditions.

It is vital for long-life design that post-exposure retained strength data base be generated. Up to this point all ceramic turbine components have been designed with "virgin" properties. A brief review of component experience in realistic, corrosion/erosion environments (i.e., turbine test rigs or engines) is now presented.

CORROSION/EROSION - TURBINE TEST RIG RESULTS

Corrosion/erosion behavior of ceramic components have either been explicity investigated (as in the Solar/MERADCOM 10 kW program), or can be inferred from results during tests utilizing combustion gases (as in the Ford portion of the ARPA "Brittle Materials Design" program). These results are briefly reviewed below.

A. The Solar/MERADCOM 10 kW Turbogenerator[19]

Developmental versions of this engine utilizes HPSN either as monolithic inlet guide vanes or as trailing edges for the current metallic guide vanes. The driving force for HPSN utilization is to reduce time between overhaul resulting from dust erosion. The turbine inlet temperature is 1700 F, which is not increased when the ceramic vanes are incorporated. In order to validate the vane and vane attachment designs for incorporation into an actual engine, an engine "simulator" using a combustor rig and a nozzle assembly was utilized. An accelerated 10-hour dust erosion test and a 70-hour corrosion test were run.

The 10-hour accelerated erosion test used 43 to 74 μm Arizona road dust, which was impinged on selected vanes at a 1700 F vane temperature and 1750 ft/sec gas velocity. The results were dramatic (Figure 10) and showed the clear superiority of HPSN over the 713 LC superalloy. The 70-hour corrosion test was carried out at 1700 F, with 3 ppm of artificial sea salt injected into the gas stream. The results showed that HPSN was 27 times more corrosion resistant than 713 LC alloy, or a 0.0004-inch recession for HPSN versus 0.0011 for 713 LC.

These rig results confirmed the trends in the relative resistance of HPSN and superalloys to corrosion/erosion environments, shown by the laboratory results reported earlier in this paper.

B. Ford/ARPA/DOE Vehicular Engine

Under the ARPA "Brittle Materials Design" program (now the ARPA/DOE program, monitored by AMMRC) Ford Motor Co. has successfully run both siliconized silicon carbide combustors and stators and RBSN stators, nose cones, and shrouds for over

19. METCALFE, A. G. *Application of Ceramics to MERADCOM 10 kW Gas Turbine Engine* in Proceedings: Workshop on Ceramics for Advanced Heat Engines, Energy Research and Development Administration, Division of Conservation Research and Technology, January 1977, p. 129-136.
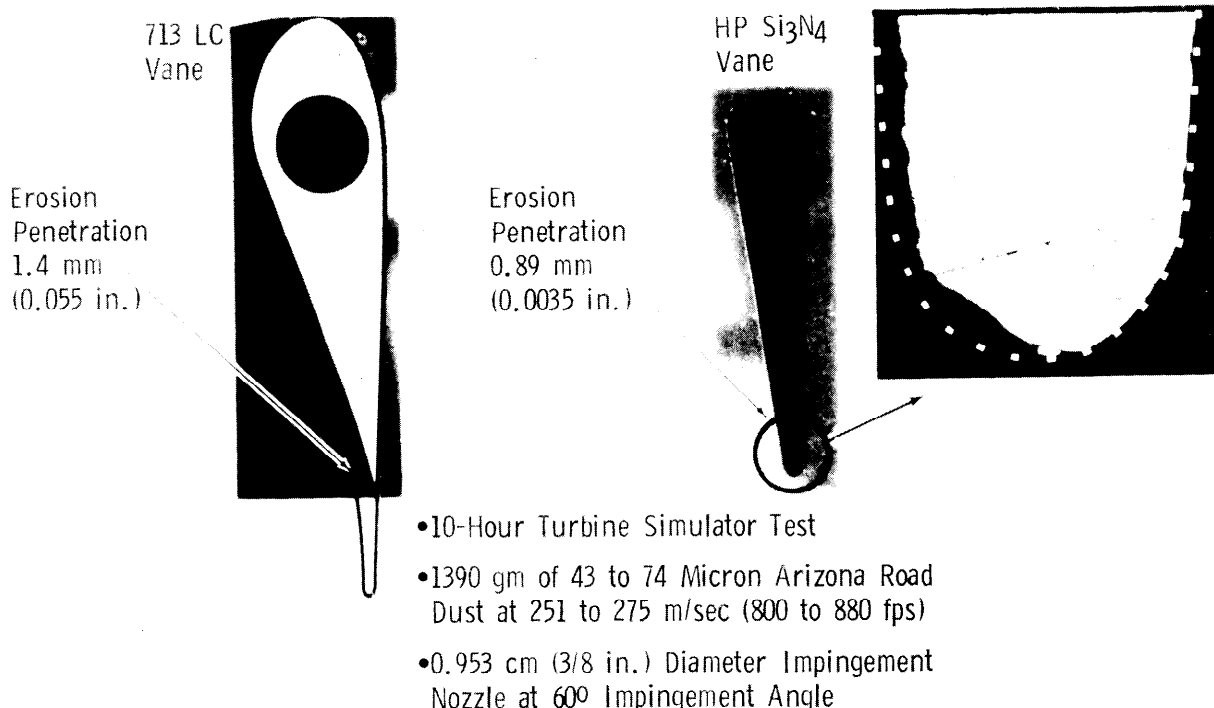
713 LC Vane

Erosion
Penetration
1.4 mm
(0.055 in.)

HP Si₃N₄ Vane

Erosion
Penetration
0.89 mm
(0.0035 in.)

●10-Hour Turbine Simulator Test

●1390 gm of 43 to 74 Micron Arizona Road
Dust at 251 to 275 m/sec (800 to 880 fps)

●0.953 cm (3/8 in.) Diameter Impingement
Nozzle at 60° Impingement Angle

Figure 10. Erosion at 1700 F.

200 hours in a rig which consisted of a Ford 820 GT engine with the rotors removed.[20] The results are summarized in Table 10. These results demonstrate that ceramic components can survive far in excess of 200 hours in realistic turbine environments.

Perhaps more important than these notable successes (for the purposes of this paper) are the relationships which the Ford investigators have elucidated between component failure and component weight gain in the rig for RBSN material.

Table 10. TESTING OF STATIONARY CERAMIC COMPONENTS IN A
FORD 820 - GT ENGINE RIG
(Reference 20)

Material	Component	Hours at 1930 F		Hours at 2500 F		Total Hr
		Actual	Goal	Actual	Goal	
Siliconized SiC	Combustor	175	175	26	25	201
RBSN	Nose Cone	175	175	26	25	201
RBSN	Stators	175	175	26	25	201
Siliconized SiC	Stator	176	175	29	25	205
RBSN	Shrouds	175	175	26	25	201

20. McLEAN, A. F., and BAKER, R. R. *Brittle Materials Design, High Temperature Gas Turbine.* Ford Motor Co., Contract DAAG46-71-C-0162, Interim Report, AMMRC TR 78-14, March 1978.

Figure 11 shows early data on Ford 2.55 g/cc RBSN relating weight gain and stator lifetime in an engine rig.[21] Figure 12 shows more recent results for newer 2.7 g/cc RBSN components (both stators and nose cones).[20]
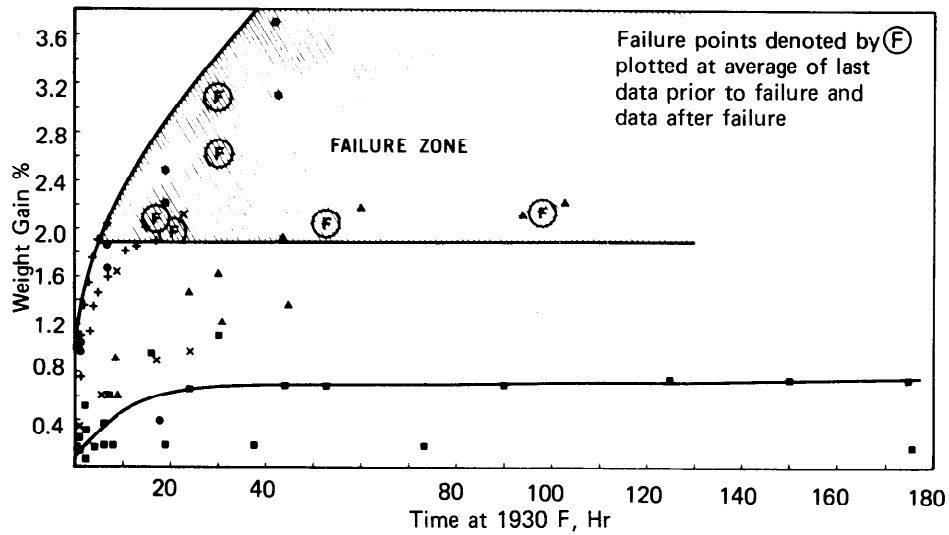

Figure 11. Weight gain versus engine rig test time at 1930 F for Ford 2.55 g/cc density RBSN stators showing failure zone (Reference 21).
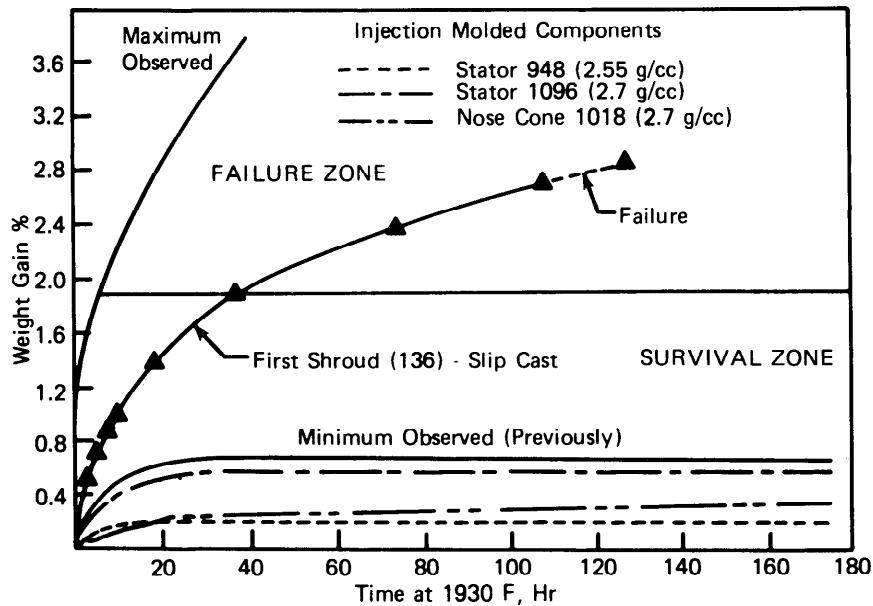

Figure 12. Weight gain versus engine rig test time at 1930 F for Ford 2.55 and 2.7 g/cc RBSN stators showing failure and survival regimes.

21. McLEAN, A. F., and FISHER, E. A. *Brittle Materials Design, High Temperature Gas Turbine.* Ford Motor Co., Contract DAAG46-71-C-0162, Interim Report, AMMRC CTR 77-20, August 1977.

While the investigators at Ford do not offer a mechanism for the weight gain, the porosity and previously observed oxidation weight gain behavior of RBSN would lead one to speculate that the gain is due to oxidation. The observation that the weight gain of the reaction-sintered SiC in the same test was negligible[20] lends support to this speculation. This correlation between oxidative weight gain and component performance has obvious implications as a component qualification and NDE technique for RBSN.

ENGINE TEST RESULTS

In the past 2 years there have been three tests of ceramics in gas turbine engines, each of which was in its own way an important first.

A. Solar/MERADCOM 10 kW Engine

This small turbogenerator engine was the first engine the author is aware of to have accumulated significant time (50 hr) with ceramics in an aerodynamically functional role. As the application of ceramics here was erosion resistance, not fuel economy, no increase in TIT was incorporated, and therefore, the power output of this engine was the same with and without the ceramic nozzles.

B. Ford/ARPA/DOE - Vehicular Engine

This engine has provided the first demonstration of an aerodynamically functioning ceramic rotor. The duodensity Si_3N_4 rotor ran in the engine for 36-1/2 hours at temperatures ranging from 2200 F to 2500+ F (1-1/2 hours at 2500+ F) and speeds of 40,000 to 50,000 rpm. This run also included ceramic nose cones, stators, shrouds, and spacers. It was thus also the first demonstration of the successful integration of stationary and dynamic ceramic components in an operational engine environment. Finally, it was the first demonstration of ceramics operating uncooled in an engine at temperatures in excess of those possible with uncooled superalloys.

C. DDA 404-3 Engine (DOE)[22]

The Detroit Diesel Allison division of General Motors is demonstrating the application of ceramic components in their 404/505 engines for truck and bus application. They are currently operating a modified 404 engine with ceramic (KT SiC) first-stage vanes at 1900 F. This engine has accumulated over 1000 hours of running to date, of which approximately 800 hours have been at 1900 F. This is the first engine to have demonstrated ceramic aerodynamic components for 1000 hours.

Based on these three engine tests the outlook for ceramics in the gas turbine is positive. Thus far, no unexpected corrosion/erosion behavior has been

22. Division of GM, Results to be presented at the 14th DOE Highway Vehicle Systems Contractors Coordination Meeting, Troy, Michigan, May 9-11, 1978.

encountered. However, no one has investigated the mechanical properties of components before and after engine (or engine rig) test to see if there is any change due to exposure.

CONCLUSIONS

Although the data on retained strength after environmental exposure from any given test program are very sparse and although there are very large gaps in the data base, when one looks at all available data a pattern does begin to emerge. Therefore, one can make several conclusions.

First, the available data indicates that in general (RBSN being the exception) Si_3N_4 and SiC ceramics have excellent erosion resistance.

Secondly, exposure to oxidative environments at 2000 F and higher and hundreds of hours in general (HPSiC being the exception) degrades the "virgin" materials strength.

Third, rig and engine tests to date have been extremely encouraging and show that uncooled ceramics are capable of operating in environments beyond the capabilities of uncooled metals.

The above review of the existent corrosion/erosion data base also leads to certain obvious recommendations.

First, any program of environmental exposure of laboratory specimens should be done on samples which are suitable for a mechanical test program, which allows a before and after exposure comparison. Also the number of specimens should be sufficiently large so that statistical inferences may be drawn.

Secondly, since laboratory tests cannot in fact duplicate engine operation experience, before and after exposure tests should be carried out on actual components. Although the number of components should allow for some statistical analysis.

Third, in view of the fact that in some cases one has only 4-6 samples to draw conclusions from, many more tests (and tests for longer times) are required.

ACKNOWLEDGMENT